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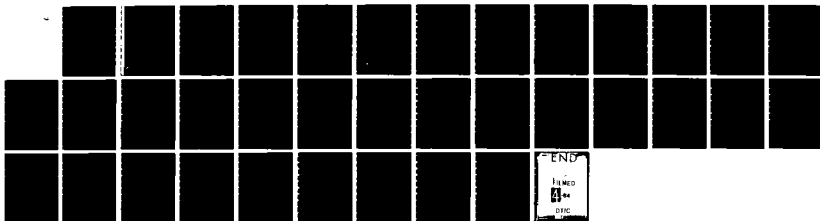
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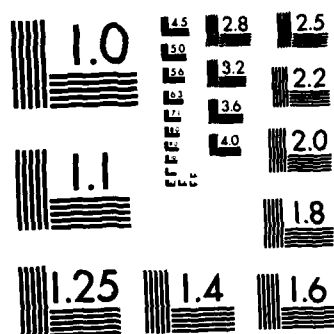
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ULTRASONICS RESEARCH LABORATORY

DEPARTMENT OF CHEMISTRY
JOHN SCHOFF MILLIS SCIENCE CENTER
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO 44106

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TECHNICAL REPORT NO. 50

COMPRESSIBILITY OF COLLOIDS: II. COMPRESSIBILITY STUDIES OF
TRI-BLOCK NON-IONIC POLYMERS IN, TOLUENE AND WATER SOLUTIONS

by

M.A. Barrett-Gultepe, M.E. Gultepe

J.L. McCarthy and E.B. Yeager

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Ultrasonic Research Laboratory

and

Case Laboratories for Electrochemical Studies

Case Institute of Technology

Case Western Reserve University

Cleveland, Ohio 44106

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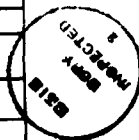
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that dissolved in toluene showed near ideal behavior enabling us to determine intrinsic compressibilities of hydrophobic and hydrophilic blocks as 4.9×10^{-11} dyn/cm² and 3.9×10^{-11} dyn/cm² respectively. The volume fraction of the bound water per segment of poly (ethylene oxide) is estimated and found to be dependent on the segment population. The mathematical treatment presented in this paper stems from that of Shiio, but goes further to define possible limits to the true compressibility, volume and density of bound water rather than making the assumption that no contraction of the water occurs.

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I. Introduction

In part I of this series¹ we have shown that an association-dissociation type chemical reaction between colloid and counter ion may give rise to an additional dispersive contribution to the adiabatic compressibility of a colloidal dispersion. Coating the particle-electrolyte interface with an amphiphilic polymer decreased this excess compressibility presumably by suppression of an association-dissociation type chemical reaction due to dipole-ion interactions between polar moieties of the adsorbed block co-polymer and the ionic end groups of the polymer colloid. However, the decrease may also be explained on the basis that the amphiphilic polymer is strongly adsorbed on the basically hydrophobic particle surface with its hydrophobic segments anchored to the surface, resulting in a more rigid structure. The use of an interface with net ion charge should be avoided for such studies if one wishes to determine the compressibility of adsorbed polymers unambiguously.

A liquid-liquid interface may be considered an ideal substrate for such studies. Emulsions with high surface area of oil-in-water (o/w) or water-in-oil (w/o) of various immiscible liquids can be prepared with amphiphilic polymers to be studied as emulsifiers. Selection of a stable (in the sense of colloidal stability) model system for a high surface area liquid-liquid interface is not simple.

Micro-emulsions and macro-emulsions prepared with mixed surface active and ionic surface active agents were excluded as

model systems. Ionic surface active agents may exhibit a chemical relaxation between counter-ions and polar heads and hence complicate the measured compressibility.

In the study to be reported in part III of this series of studies, non-ionic block co-polymers of poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide), A - B - A tri-block type (the hydrophobic portion in the center and the hydrophilic portions at both ends) were used as emulsifier for toluene in water emulsions. Their ample solubility in both toluene and water facilitates acoustic study of their behavior (compressibilities) in either medium. At the present time, knowledge concerning the conformation of non-ionic copolymers at the oil/water interface is very limited.

However it is generally assumed^{2,3} that interactions between the hydrophilic and hydrophobic portions of the emulsifying molecule not only determines the radius of curvature of the oil/water dispersion, it also determines the stability of it. Therefore, it will be very informative to study the interaction between oil and water soluble segments of the emulsifier by measuring their compressibilities in both liquids as a function of concentration. These results are presented here as part II of this series.

The compressibilities of water and oil soluble portions of the emulsifier can then be compared with the three dimensional surface compressibilities of the emulsion globules prepared with the same emulsifier.

II. Theoretical

The apparent molar compressibility (adiabatic) of a solute ϕ_K is defined as:

$$\phi_K CV' = \beta V' - \beta_0 V_0' \quad (1)$$

where C is the concentration of the solute as moles/liter, β is the compressibility of the solution, V' is the volume of the solution, β_0 is the compressibility of the pure solvent and V_0' is the volume of the solvent if its density were that of the pure state. This is related to the specific apparent compressibility ϕ_k by:

$$\phi_K C \equiv \phi_k c \quad (2)$$

where c is the concentration of the solute in grams/cm³. We can write

$$V' \phi_K c + V' \beta_0 = \beta V' \quad (3)$$

Dividing the above equation by the total volume of solution and substituting $\beta_{app} \cdot \phi_v$ for ϕ_k , where β_{app} is the apparent compressibility of the solute, we obtain:

$$c \beta_{app} \phi_v + V_0 \beta_0 = \beta \quad (4)$$

V_0 is the volume fraction of solvent and can be determined from $V_0 = (\rho - c)/\rho_0$, while β can be determined from the velocity U and density measurements by means of $\beta = 1/(\rho U^2)$.

Following Shiio's model⁴ considering the compressibility of the bound water β_2 and true compressibility β_1 and true volume V_1' of solute, the total volume V' of the solution can be written as:

$$V' = V_0' + V_1' + v_2' - v_0' \quad (5)$$

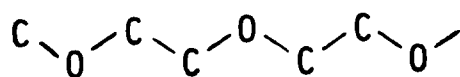
A portion of the solvent of volume v_0' will be attached to the solute and compressed to a smaller volume v_2' . Using the same line of thought for the corresponding compressibilities, and again converting volumes (primed quantities) to volume fractions, eq (4) can be written as:

$$\beta_{app} c \phi_v + \beta_0 V_0 = \beta = V_1 \beta_1 + V_0 \beta_0 + v_2 \beta_2 - v_0 \beta_0 \quad (6)$$

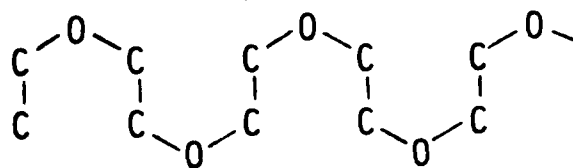
The left hand side of the above equation expresses the total compressibility of the solution in terms of normal solvent, while the right hand side expresses it in terms of bound and unbound solvent as well as true compressibility and volume fraction V_1 of the solute.

In Shiio's treatment, the solute molecule was treated as a whole. However, in our case, the solute consists of an A - B - A type, tri-block co-polymer. The A type block is poly

ethylene oxide. There is considerable evidence in the literature^{5,6} that the interaction between ethylene oxide groups and the water molecules causes a complete conformation change from zig-zag shaped linear polymer strands to what is referred to as "meandering form". The equilibrium angles between the bonds are retained, but the overall length of the strand is considerably contracted (by about 50%). This contraction probably has associated with it a decrease in volume of the molecule. Therefore the meandering structure may show smaller compressibility.



Zig Zag Form



Meandering Form

Although Rosch⁵ or Schonfeldt⁶, in their description of the two conformations, did not discuss compressibility, it is anticipated that the bound water molecules associated with this "meandering structure" will exhibit a smaller compressibility than the unbound and weakly associated water.

If the polymer solution shows ideal behavior when dissolved in a solvent, such as toluene, the apparent molal compressibility of the polymer can be considered the intrinsic compressibility of the substance. If the subscripts A and B refer to poly(ethylene oxide) and poly(propylene oxide) respectively, the volume fractions V_A , V_B and compressibilities

β_A , β_B of the blocks can be determined by velocity and density measurements on solutions of a series of polymers with varying proportions of poly(ethylene oxide) content. A value for β_B can be obtained by extrapolating the measured compressibility value to 0% POE content. Similarly the β_A value is determined by extrapolating the compressibilities to 100% POE content.

The total specific apparent compressibility of the above mentioned "zig-zag structure" can be expressed as:

$$\phi_k (\text{zig-zag}) = (V_A \beta_A + V_B \beta_B) \quad (7)$$

As we will show in the results section, solutions of these polymers in toluene fulfilled the conditions of a nearly ideal solution, and the intrinsic compressibility of the polymer was thereby determined.

This treatment of data is not valid for aqueous solutions of these polymers. Attempts to obtain V_A and β_A similarly by extrapolating to 100% POE suffers from the complication of the change of form; zig-zag structure to meandering. The meandering structure appears to be more compact than the zig-zag structure and may have a lower compressibility. It is impossible, however, to decide just how much of the change in volume and compressibility is associated with the polymer as compared with that caused by the change in the water structure surrounding the polymer.

The total specific apparent compressibility of the meandering structure can be expressed as;

$$\phi_k \text{ (meandering form)} = V_A \beta_A + V_B \beta_B + v_2 \beta_2 - v_0 \beta_0 \quad (8)$$

In this case β_A and V_A values are not necessarily the same as in the previous case (polymer dissolved in toluene). Rearranging eq.(6) and dividing by β_0 the following equation is obtained.

$$\frac{1}{\beta_0} (\beta - \beta_0 V_0 - \beta_1 V_1) = v_0 (1 - \frac{v_2 \beta_2}{v_0 \beta_0}) \quad (9)$$

Although it is not possible to determine uniquely the volume fraction and compressibility of all the components, a great deal of further qualitative information can be derived. We may suppose V_A and β_A retain the values found in toluene and all the bound water (strongly and loosely bound) is considered together. The measurements then give a value for $v_0 (1 - \frac{v_2 \beta_2}{v_0 \beta_0})$ through eq.(9). In his treatment Sniiio assumed β_2 to be the same as ice (1.8×10^{-11} dyn/cm²). In fact definite upper and lower limits can be set for β_2 in that it must be greater than 0, and second, as β_2 is assumed to approach β_0 , the resulting calculated v_2 and v_0 increased to infinity. Since no volume fraction can be greater than 1, this effectively sets the upper limit as: $\beta_2 \leq \beta_0 + (V_0 - v_0 + v_2) \beta_0 + V_1 \beta_1 - \beta$. The value of β_2 also determines the value of the density of the bound water through the relationship expressing volume average of the densities.

$$V\rho = V_1 \rho_1 + V_0 \rho_0 + v_2 \rho_2 - v_0 \rho_0 \quad (10)$$

where $\rho, \rho_0, \rho_1, \rho_2$ are the densities of the solution, pure water, solute, and bound water respectively.

III. Experimental

Sound velocity measurements were made at 2 MHz with a Schall interferometer. All velocity measurements were performed at 25°C. The temperature was kept constant during measurements within $\pm 0.02^\circ\text{C}$. Description of the interferometer and the measurements can be found in part I of this series. The velocity results were obtained in the polymer solutions with the accuracy of 0.001% for toluene, and 0.01% for water when used as solvents. The density of polymer solutions as a function of polymer concentration were measured with a Mohr balance to 0.1%. A series of tri-block type non-ionic block co-polymer of poly(ethylene oxide) were obtained from BASF Wyandotte Corporation U.S.A., under the commercial name of Pluronic[®] polyols. The Pluronics of the code, Pl03, Pl04, Pl05, P75 and Fl08, F68, F38 and L62 were used during this study. The first letters P, F and L denote paste, flakes and liquid respectively. The last digit of every Pluronic multiplied by 10, gives its approximate % poly(ethylene oxide) in the total molecule, while the preceeding digits are a code for the molecular weight of the poly(oxypropylene). The average molecular weights range from 2,000 to 14,000 was studied. The manufacturer did not provide any information about the distribution around the average molecular weight of a given Pluronic.

Commercial ethylene oxide condensation products may show either a narrow or wide distribution of molecular weights for each block depending on the conditions of manufacturing. It was found during the solution preparation of Pluronics in water and toluene that while some Pluronics contain toluene insoluble fractions, some others contain water insoluble materials. For example, Pl03 yields complete solution in water, while it left an estimated 2% of the total weight insoluble residue in toluene. We attribute this behavior to a distribution of molecular weight of these samples. All Pluronics were used without further purification or fractionation.

IV. Results and Discussion

Solutions of various Pluronics were made using toluene and water as solvents, each in a range of concentrations generally from 1 g Pluronic/liter to 200 g/liter. The densities of these solutions were measured at a constant temperature. Within the accuracy of our measurements, ($\pm 0.001 \text{ g cm}^{-3}$) the density of polymer solutions in both water and toluene varied linearly with concentration. However, a comparison of the density measurements in the two solvents yield significantly different apparent specific volumes. The density values given by the manufacturer for the pure Pluronics are in reasonable agreement with those determined in toluene. The results are given in Table I. The smaller specific volume in water reflects the fact that either there is water in compressed state associated with the

hydrophilic portion of the molecule or the "meandering structure" takes up a smaller volume. In the zig-zag structure the former is likely to be the main contributor to this effect.

TABLE I

The apparent specific volumes, ϕ_v (cm³/g) of various Pluronics in water and toluene and in pure form. Unless otherwise stated these are for 25°C.

Pluronics	molecular_wt	%_POE	ϕ_v (water)	ϕ_v (toluene)	ϕ_v (pure)
P103	4950	30	0.932	0.957	0.96*
P104	5850	40	0.913	0.948	0.96*
P105	6500	50	0.914	0.940	0.95*
F108	14000	80	0.866	-----	0.94**
F38	5000	80	0.860	-----	0.93**
F68	8350	80	0.866	-----	0.94**
P75	4150	50	-----	0.942	0.94*

* calculated from density values given at 60°C

** calculated from density values given at 77°C

Taking a series of Pluronics with varying fractions of poly(ethylene oxide), (or POE) we can extrapolate the reciprocal specific volume results to obtain the apparent specific volumes of pure POE and pure poly(oxypropylene) (POP) as shown in Fig. 1

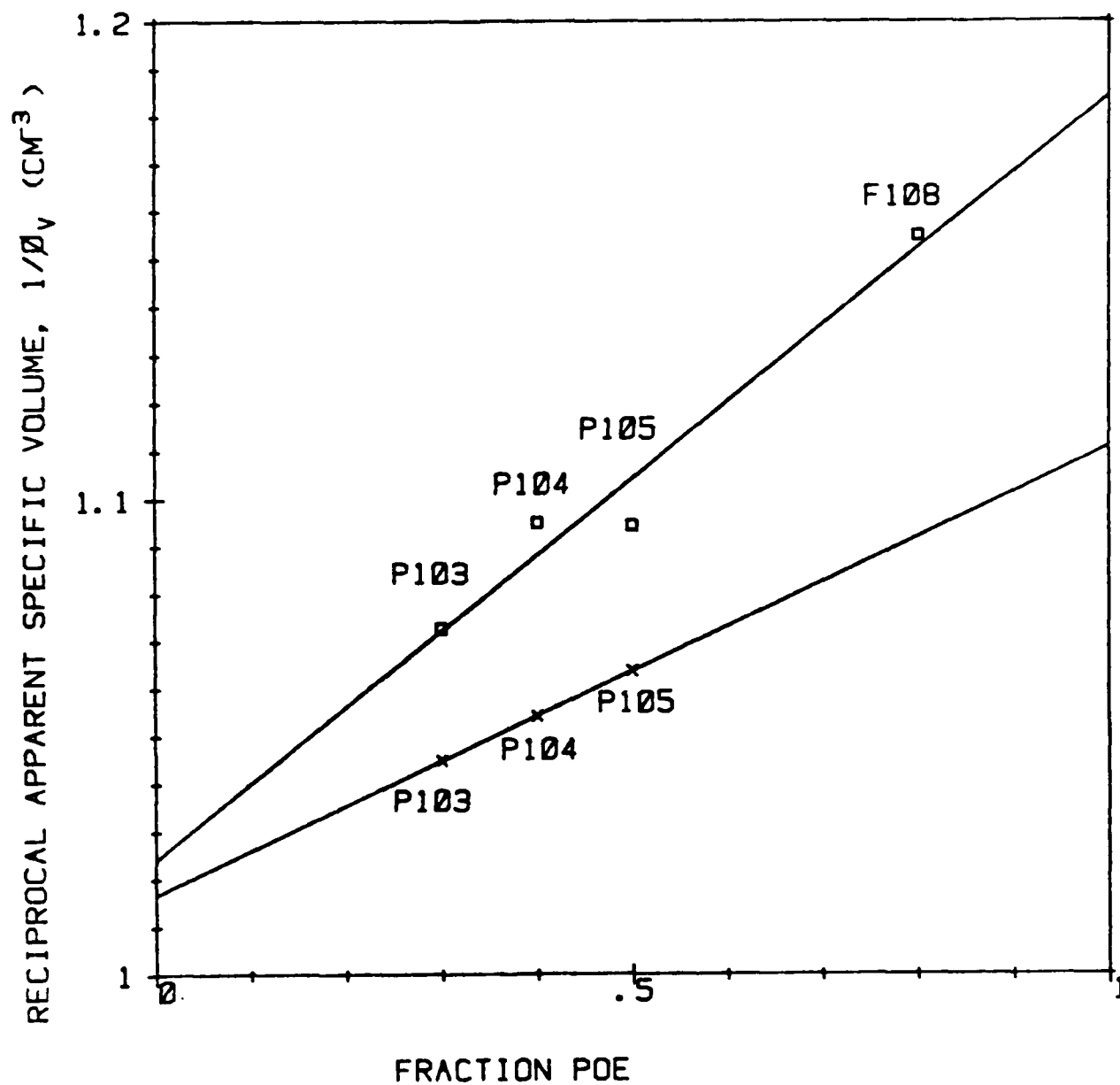


Fig. 1. Reciprocal apparent specific volume, $1/\phi_v$, of various Pluronic in water (upper curve) and toluene (lower curve) as a function of poly(oxyethylene) fraction in the polymer.

for both water and toluene. The extrapolated values representing the pure POP should ideally be the same in both toluene and water, no interaction is expected between POP and toluene. However, velocity measurements on solutions of Pluronics in toluene have shown that there is a small but observable interaction between toluene and Pluronics. The extrapolated values of $1/\phi_v$ from toluene and water solutions, or "apparent density", of POP are 1.0168 and 1.0243 g/cm³, or in terms of apparent specific volume, 0.9834 and 0.9763 cm³/g respectively. Likewise extrapolating to pure POE we find densities of 1.1108 and 1.1843 g/cm³ for toluene and water respectively, or 0.9003 and 0.8444 cm³/g respectively.

The velocity of sound at 2 MHz as a function of concentration of Pl05 and Pl75 in toluene are given in Fig. 2, along with the theoretical curve assuming ideal behavior; i.e. taking volume average densities and compressibilities. It can be seen that the fit of the experimental data to the theoretical curve are good, but not perfect. All the other Pluronics dissolved in toluene used in this study gave similar curves.

The data can also be represented by plots of apparent compressibility β_{app} as a function of concentration, as in Fig. 3. The scatter of points at the low concentrations is due to the fact that small errors in density or velocity measurements are magnified in such compressibility plots. The apparent compressibilities of the solutes are essentially constant at concentrations up to 250 g/liter, indicating near ideal behavior.

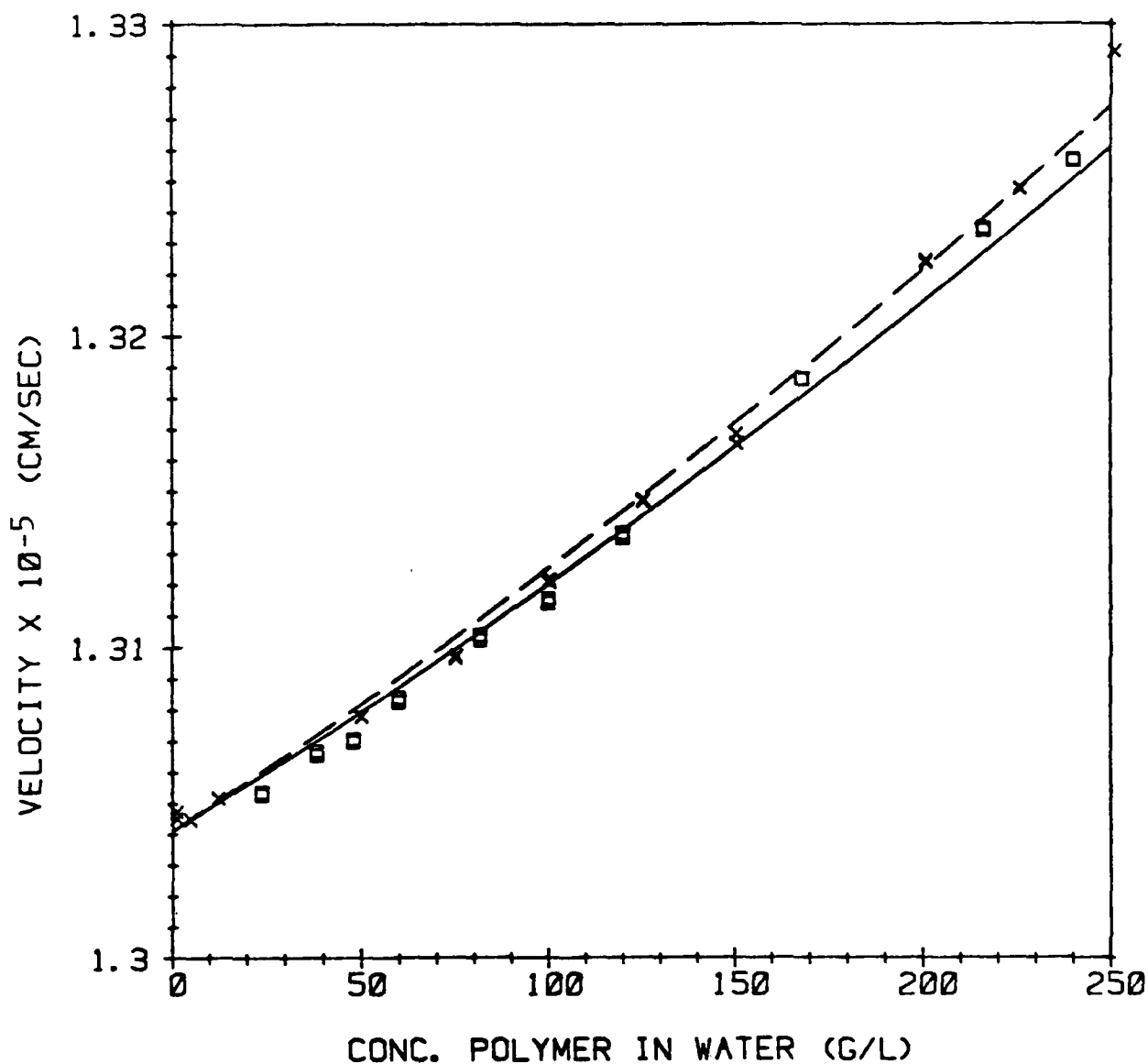


Fig. 2. The velocity of sound at 2 MHz as a function of concentration of P105 and P75 in toluene, along with the theoretical curves assuming ideal behavior. Calculations were made taking volume average densities and compressibilities. Solid line: theoretical curve for P105, dashed curve for P75. Experimental points: \square -P105, X-P75.

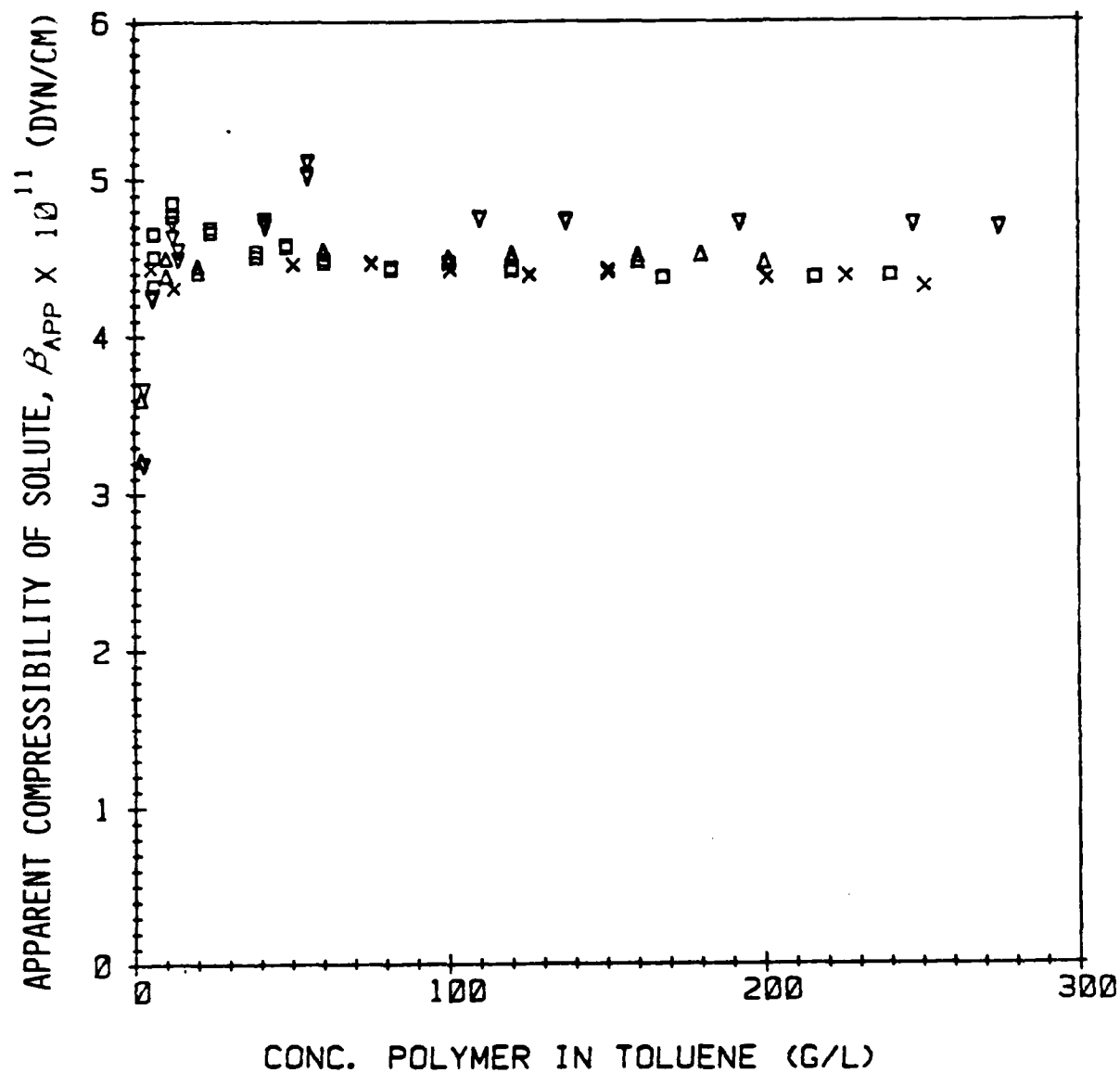


Fig. 3. Apparent compressibility, β_{app} of various Pluronics in solutions of toluene as a function of concentration.
 \square -P105, Δ -P104, ∇ -P103, X-P75.

The velocity data for solutions of Pluronics in water are treated similarly. An example of velocity versus concentration of P105 is shown in Fig. 4. Unlike the toluene data, deviation from ideal behavior is very pronounced. The shape of the velocity curve is typical for molecules showing solute-solute and solute-solvent interactions, such as solutions forming micelles.

The plots of apparent compressibilities of P103, P104, P105 and P108 are given in Fig. 5. Excluding P108, the others show a steep rise with concentration up to about 40 g/liter, which tails off at high concentrations. In the high concentration region there is a trend towards higher compressibility with decreasing POE content in the molecule. Laser light scattering results on a sample of P105 at a concentration of 40 g/liter in water indicated formation of monodispersed aggregates of 250 Å diameter. As polymer containing POE comes in contact with water it immediately converts from zig-zag form to "meandering structure", incorporating strongly bound water of reduced compressibility. This behavior is unique⁶ to POE with the minimum polymerization number of 9. The Pluronics which have been investigated all have at least 15 contiguous segments. In addition to this tightly bound water it is reasonable to assume the presence of more loosely bound water. It is also assumed that POP interacts much less with water since Pluronics with less than 20% POE do not dissolve in water. As the concentration of polymer is increased, the POP portions of the molecules will associate. This results in micelle - like

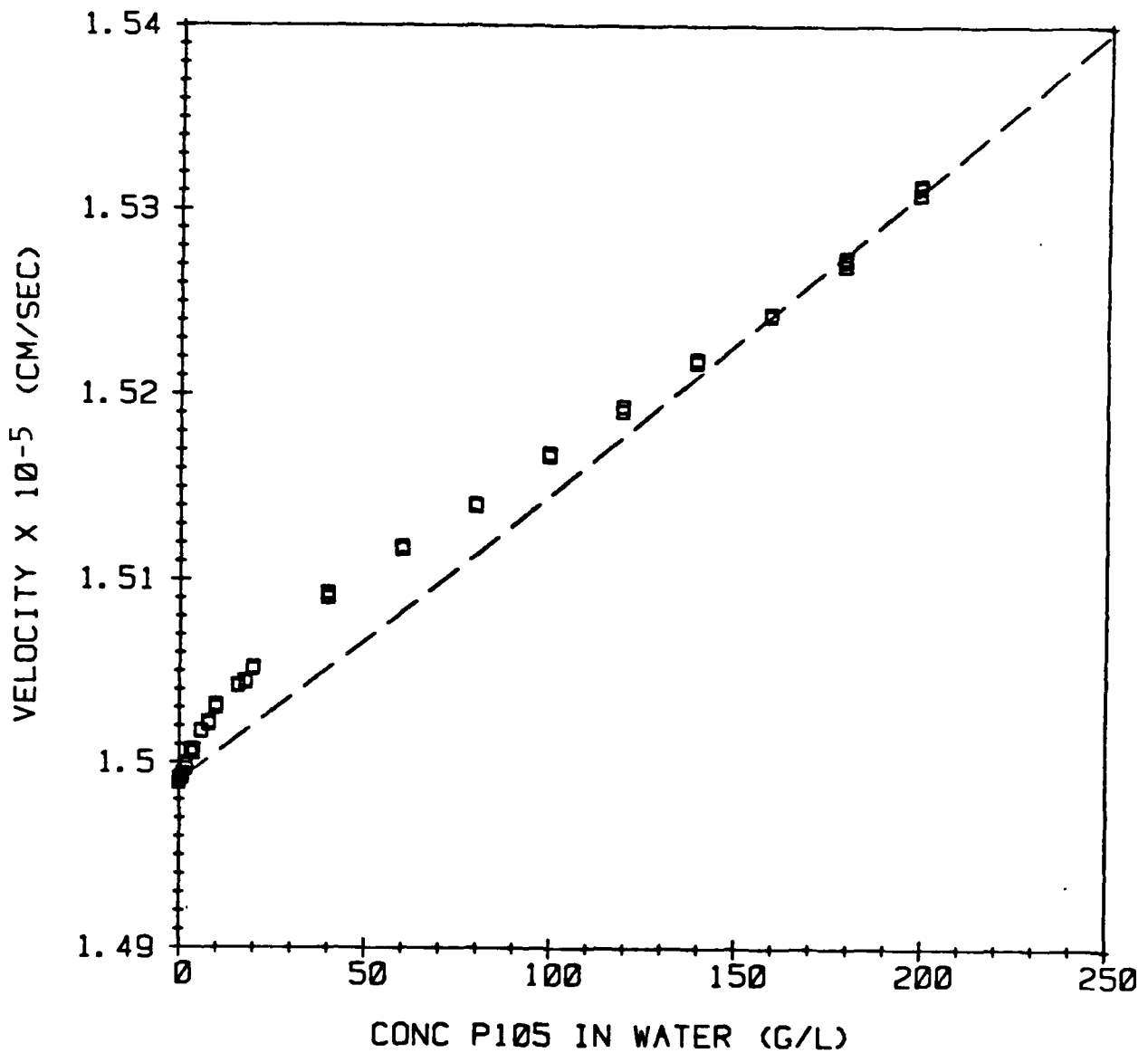


Fig. 4. The velocity of sound at 2 MHz as a function of P105 concentration in water, along with the theoretical curve assuming ideal behavior. Calculations were made taking volume average densities and compressibilities.

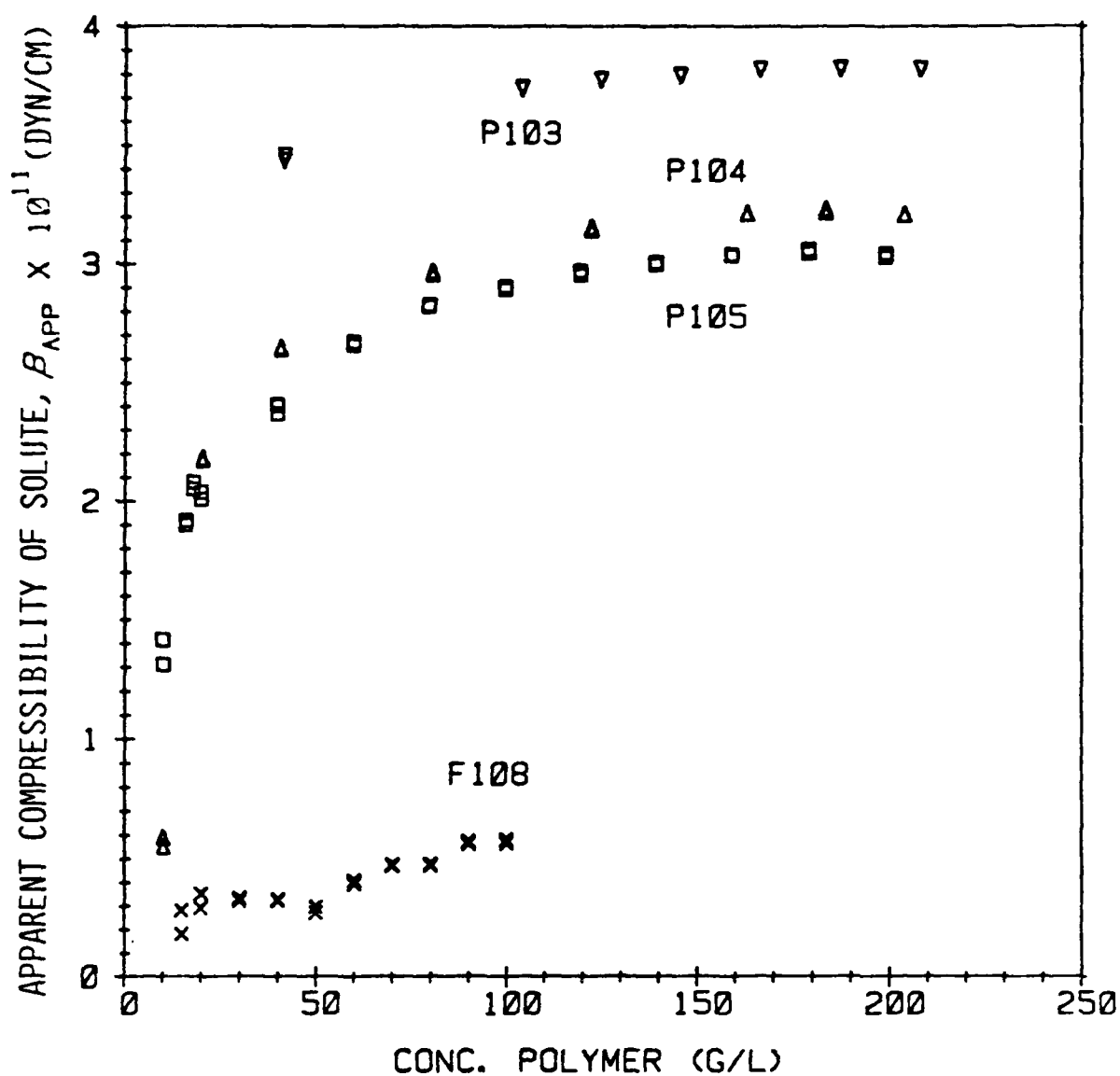


Fig. 5. Apparent compressibility, β_{app} of various Plur-
onics in solutions of water as a function of concen-
tration. Compressibility values obtained at 2MHz,
25°C.

aggregates, with the POP's inside and POE segments protruding out into the water phases.

There has been some conflicting evidence reported in the literature^{7,8} as to whether micelles form in aqueous solutions of the Pluronics, including those involved in this present study. Schmolka⁷ has concluded, mainly on the basis of dye absorption experiments, that micelles form, with the CMC (critical micelle concentration) at around 0.3 g/l. Pluronics containing 80% POE (such as F38, F68 and F108) only form dimers⁹. In this work, velocity measurements were made on aqueous solutions of these polymers as a function of concentration and the δ_{app} curve vs. concentration (see Fig. 6) showed no evidence for aggregate formation. At very high concentrations, X-ray diffraction studies show that water molecules contribute to an interaction between POE chains, forming lammellar or cylindrical structures^{10,11}. The viscosity reaches a maximum when the ratio of water molecules to oxygen of the POE segments is approximately 2 to 1¹². During the aggregation process much of the loosely bound water is squeezed out, but tightly bound water incorporated in the meander structure will remain. As is normal for micellar solutions, increasing the concentration of polymer molecules beyond the critical micelle concentration increases the number of aggregates but not their size or structure, while the concentration of unassociated polymer molecules remains virtually constant and becomes insignificant compared to aggregates. Thus the proportion of tightly bound to loosely

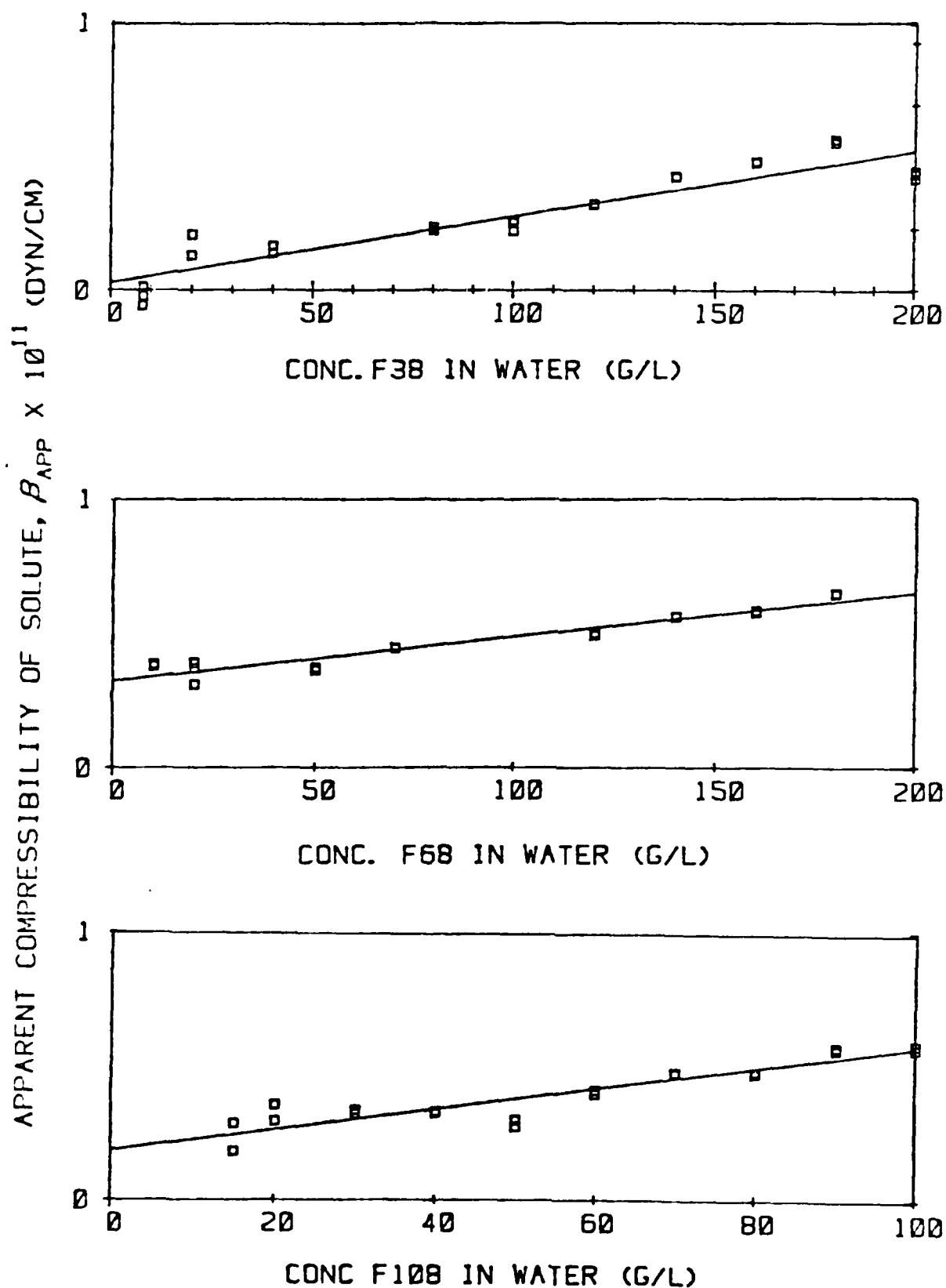


Fig. 6. Apparent compressibility β_{app} of several Plur-
onics containing 80% POE, in aqueous solutions as a
function of concentration.

bound water increases and levels off at higher concentrations.

F108 differs from the others due to the fact that 80% of the polymer consists of POE. At concentrations above 100 g/liter it forms gels and meaningful measurements cannot be performed. From Fig. 5 there appears to be less interaction between F108 molecules within the concentration range in which velocity measurements were performed. Other Pluronics with 80% POE (F38 and F68) were found to be similar in this respect (Fig. 6) reinforcing the conclusion of Cowie⁹.

For Pl03, Pl04 and Pl05 polymers, the high concentration apparent compressibility values are extrapolated to infinitive dilution using the data of Fig. 3 and Fig. 5. This is done so that one can eliminate the contribution due to the aggregate - aggregate interaction. This is a minor effect in toluene. Along with these values, the intercepted compressibilities for all three polymers from toluene solutions data are plotted as a function of POE percentage. Results are given in Fig. 7. Both sets of points fall on straight lines. For zero percent POE block, both lines merge at the same intercept of 4.9×10^{-11} dyn/cm² of apparent compressibility. The compressibility value for POE segments can be obtained in principle from the intercept of the toluene data line to 100% POE, which yields 3.9×10^{-11} dyn/cm². We believe that this value represents the compressibility of the zig-zag formed POE, in the absence of water molecules. The volume average of these compressibilities yield the intrinsic compressibility of the POE-POP-POE tri-block co-polymer. The interpretation of the intercept of the line at

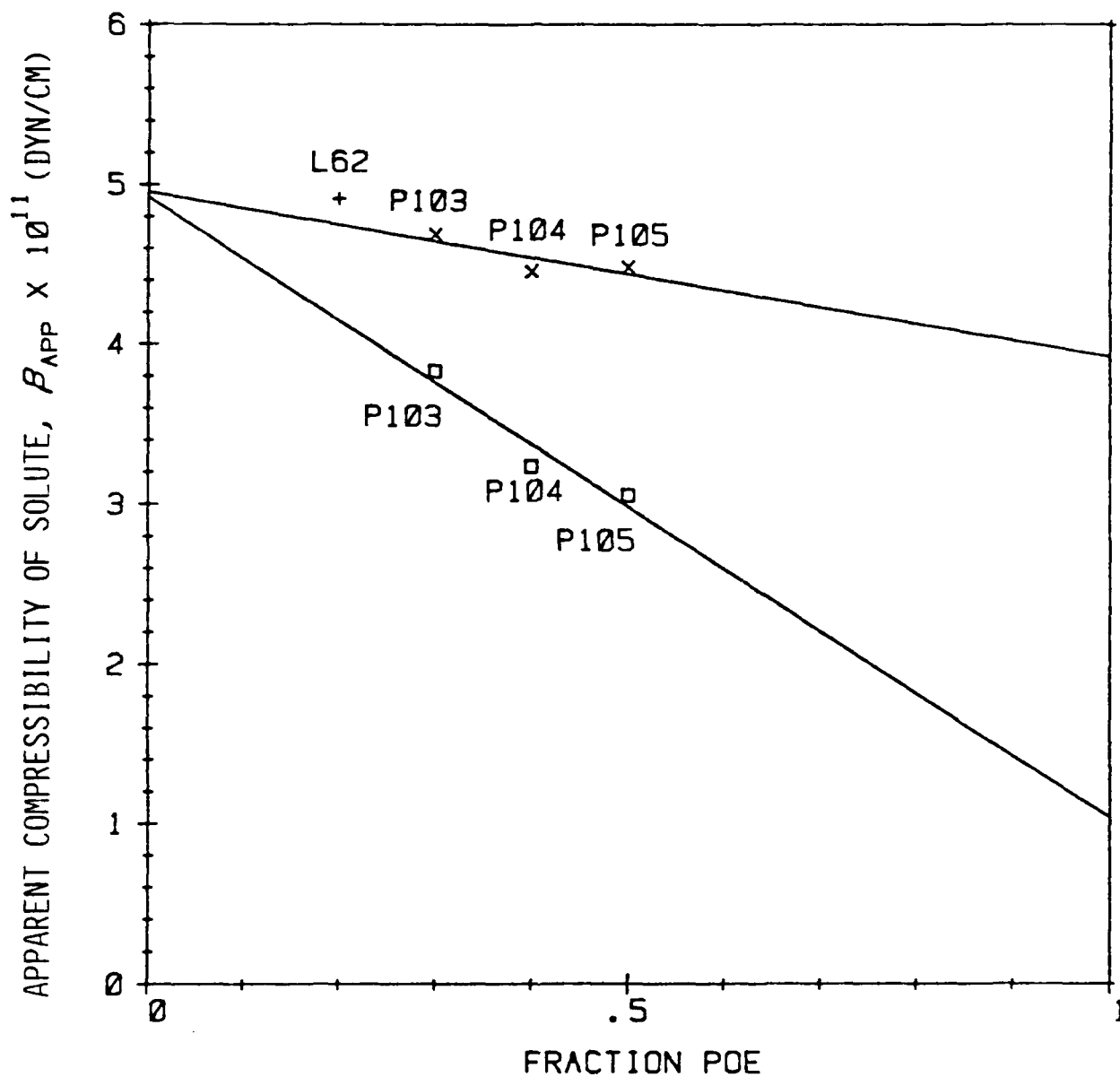


Fig. 7. High polymer concentration compressibility values extrapolated to infinite dilution for Pluronics with various poly(ethylene oxide) POE, fractions. X and \square represents toluene and water solutions respectively. The data point + is for another Pluronic L62 which, being in the liquid state, could be measured in pure form.

the 100% POE for water solutions is not so clear cut, but can be considered to give the value of the apparent compressibility of the meander structure of POE which includes its tightly bound water, along with the amount of loosely bound water associated with aggregates. On the assumption that there is no alteration of volume and intrinsic compressibility on conversion to the meander form, the quantity $v_0 \left(1 - \frac{v_2 \beta_2}{v_0 \beta_0} \right)$ was calculated for all the aqueous solutions from the measurements. If we assume that the bound water has the compressibility of ice, i.e. 1.8×10^{-11} dyn/cm², corresponding values of v_2 can be estimated per segment of POE. These are plotted in Fig. 8. Ideally the v_2 values for various Pluronics might be expected to coincide. The fact that the Pluronics with higher percentage of POE will have the longest chain length protruding in the water, i.e., in a configuration less densely packed results in it retaining more loosely bound water.

The possible range of β_2 is from 0 to 4.2×10^{-11} dyn/cm² as explained in the previous section leading to a possible range of v_2 from 3.97×10^6 to 7×10^{-2} cm³ per segment. This further defines a possible range of densities, ρ_2 , for the total bound water, from 1.0025 to 1.090 g/cm³.

V. Conclusion

Ultrasonic compressibility measurements are very sensitive to the molecular configurations of the tri-block non-ionic co-polymers in solvents showing ideal and non ideal behavior.

Fig. 8. Volume of bound water per gram of poly(ethylene oxide) as a function of concentration of various Pluronics, assuming the bound water has the compressibility of, 1.8×10^{-11} dyn/cm².

The Pluronics studied in this work showed a very pronounced non-ideal behavior in aqueous solutions indicating aggregate formation. This is confirmed by laser light scattering measurements. Those polymers that dissolve in toluene showed near ideal behavior enabling us to determine intrinsic compressibilities of hydrophobic and hydrophilic blocks. The volume fraction of the bound water per segment of poly(ethylene oxide) is estimated and found to be dependent on the segment population. The treatment presented in this paper stems from that of Snio, but goes further to define possible limits to the true compressibility, volume and density of bound water rather than making the assumption that no contraction of the water occurs.

LIST OF SYMBOLS

- C = Concentration of the solute as moles/liter
- c = Concentration of the solute as grams/cm³
- U = Velocity of sound in the solution
- V' = Volume of the solution
- V'_0 = Volume that would be taken up by equal amount of pure solvent
- V_0 = Volume fraction of V_0
- V'_1 = True volume of solute
- V_1 = True volume fraction of the solute
- v'_2 = True average volume of the bound water
- v_2 = True average volume fraction of the bound water
- v'_0 = Volume of the same amount of unbound water
- v_0 = Volume fraction of v'_0
- V_A = Volume fraction of poly(ethylene oxide)
- V_B = Volume fraction of poly(propylene oxide)
- β_{app} = Apparent compressibility of solute
- β_1 = True adiabatic compressibility of the polymer
- β_0 = Compressibility of the pure solvent
- β_2 = Volume average compressibility of the strongly and loosely bound water
- β_A = True compressibility of poly(ethylene oxide)
- β_B = True compressibility of poly(propylene oxide)
- ρ = Density of solution
- ρ_0 = Density of solvent
- ρ_1 = Density of the solute
- ϕ_K = Apparent molar compressibility of the solute
- $\phi_V = (\rho_0 - \rho - c)/(c \rho_0)$ apparent specific volume, cm³/g
- ϕ_k = Specific apparent compressibility of solute

REFERENCES

- 1- Barrett-Gultepe, M.A., Gultepe, M.E., and Yeager, E.B., J. Phys. Chem., 87, 1039 (1983).
- 2- Mitchell, J.D., and Ninham, B.D., J. Chem. Soc. Faraday Trans. II, 77 (1981).
- 3- Mukherjee, S., Miller, C.A., and Fort, T. Jr., J. Colloid Interface Sci., 91, 223 (1983).
- 4- Shiio, H., Ogawa, T., and Yoshihashi, H., J. Am. Chem. Soc., 77, 4980 (1955).
- 5- Rosch, M. Kolloid-Z. 147, 79 (1956); 150, 153 (1957).
- 6- Schonfeldt, N., "Surface Active Ethylene Oxide Adducts" Pergamon Press, Oxford, (1967) p.133.
- 7- Schmolka, I.R., and Raymond, A.J., J. Am. Oil Chemists Soc. 42, 1088 (1965).
- 8- Mankowich, A., J. Phys. Chem. 58, 1028 (1954); Ball, W.E., Ibid 63, 299 (1959).
- 9- Cowie, J.M.G., and Sirianni, A.F., J. Am. Oil Chemists Soc. 43, 572 (1966).
- 10- Schulman, J.H., Matalon, R., and Coheen, M., Discussions Faraday Soc., No. 11, 117 (1951).
- 11- Tsouladze, G., and Skoulios, A., J. de Chim. Phys. 60, 626 (1963).
- 12- Rosch, M., Kolloid-Z. 147, 78 (1956).

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